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(54) Title: EXTRUDABLE CEMENTITIOUS MATERIAL

(57) Abstract: A method and agent for treating a cementitious material for extrusion, comprising adding to the cementitious material a viscosity enhancing agent and a dispersion agent in a quantity sufficient to increase the efficacy of the viscosity enhancing agent. By increasing the efficacy of the viscosity enhancing agent, extrudability may be maintained with less viscosity enhancing agent or a lower grade (cheaper) viscosity enhancing agent than is conventionally used, or the extrudability may be improved for the same quantity of viscosity enhancing agent compared to a conventional dosage.

TITLE: EXTRUDABLE CEMENTITIOUS MATERIAL**TECHNICAL FIELD**

The present invention relates to building products and particularly fibre reinforced cement building products.

5 BACKGROUND ART

Fibre reinforced cement boards and other products have been widely used as materials for walls, ceilings, roofs, floors etc: of buildings and for substitutes for wood trim, frames etc.

There are many methods for forming and shaping such FRC products including
10 Hatschek sheet process. Mazza pipe process, Magnani sheet process, injection moulding, hand lay-up, casting, filter pressing, roll forming etc.

Extrusion of fibre cement products has been performed on a limited basis but it has a number of difficulties which have reduced its commercial viability. In the extrusion process, the cementitious slurry or paste is forced through a die and the material can be
15 subjected to elevated pressures. For this reason, it is important that the slurry or paste has good flow characteristics. The cementitious formulation often contains elements that are present almost entirely as process aids, increasing the flow properties, the shape retention properties or enhancing the surface finish. A common type of these additives can be broadly classified as viscosity enhancing agents (VEA) or 'binders'. A principal
20 function of these is to increase the viscosity of the liquid phase, and to counter problems such as segregation of the liquid and solid phases ('water retention'), lack of shape retention, non uniform dispersion of the solid components etc.

For materials such as clays extruded in the brick and tile industry, the inherent good flow properties of the clay mean that the use of such VEA's may be minimised,
25 and therefore cheap. However when the solids suspensions that require forming are not plastic (such as cementitious slurries or pastes), and inherently resistant to flow, the additives are often expensive high molecular weight organic polymers. Further, the demand for viscosity enhancing agents can be increased by the presence of reinforcing fibres, especially if these are hard to disperse or do not have good water retention
30 characteristics.

Asbestos generally has better dispersion and water retention properties than pulp fibres, and when used as reinforcement in cementitious compositions, require less extensive use of viscosity enhancing agents, however, as is well-known in the art, the use of asbestos fibres is outlawed in many countries and is undesirable even in those countries where its use is legal.

Accordingly, previous efforts in finding reinforcing fibres for extrudable cementitious pastes have concentrated on non-asbestos fibres and, in particular, choosing or treating such non-asbestos fibres so that their dispersion and water retention characteristics make them suitable for use in extrusion moulding with minimal use of viscosity enhancing agents. For instance, US patent no 5,891,374 discloses a process for producing a fibre reinforced cement matrix composite. In this document, hydraulic cement, water and low quantities of water soluble binder are mixed together with synthetic fibres to produce an extruded and cured composite product. Optionally, a water reducing agent may be added to assist in preferential alignment of the fibres in the load bearing direction.

Such synthetic fibres are commonly used. However, they are expensive and some are unable to be cured at high temperatures such as in an autoclave. Currently, wood pulp fibres remain the primary fibre of choice for reinforcing cement composites for building materials, where they show excellent performance with regard to mechanical strength, toughness and durability at a low cost. However, extrudable cement compositions containing wood pulp fibres have very stringent requirements for rheology modification and require expensive high molecular weight organic polymers as viscosity enhancing agents.

It is believed that the viscosity enhancing agent performs two functions. Firstly, it acts as a high solid suspension thickener to increase the water retention properties of the slurry, and secondly, it also lubricates the suspended particles thereby allowing the high solid suspension to flow under deformation without phase separation and segregation.

The effectiveness of such a viscosity enhancing agent is believed to be a combination of three actions, namely:

adsorption of water by long-chain polymer molecules, increasing viscosity of the mixed water,

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association of adjacent polymer chains, further blocking the motion of water, and intertwining and entangling of the polymer chains, thereby behaving in a sheer thinning manner.

For suspensions involving cement and pulp fibre that are processed by extrusion, the commonly used viscosity enhancing agents are high viscosity cellulose ethers such as methyl cellulose, hydroxypropyl methyl cellulose or hydroxyethyl methyl cellulose. US Patent 5,047,086 discloses the use of extremely high viscosity (>80,000 cps @ 2% solution at 20° C) alkylcellulose and/or hydroxyalkylalkylcellulose at 0.2-1 wt % levels in the preparation of these compositions. This patent also discloses that if lower viscosity (12,000-40,000 cps @ 2% solution at 20° C) grades of these compounds (akin to those used in asbestos fibre/cement extrusion compositions) are used, much higher addition levels are required.

Even when mouldings are made with such high viscosity grade agents in an effort to minimise the quantity used, the cost ratio of viscosity enhancing agent to the total cost of the extruded moulding can be in the order of one fourth to one half. Thus it is clear that any method of reducing the cost and/or amount of viscosity enhancing agents required to attain excellent mouldability, is greatly to be desired.

In addition to the cost aspect, highly effective viscosity enhancing agents like hydroxypropyl methylcellulose (HPMC) and hydroxyethyl methylcellulose (HEMC) experience a phenomenon known as high temperature gelation. That is, the viscosity of the agent undergoes a sharp increase when the temperature exceeds a specific limiting temperature, known as the gel temperature. The gel temperature of these viscosity enhancing agents varies with the exact chemistry (i.e. degree of substitution etc.). Though this phenomenon can be useful in some applications, it is limiting in others. For example, cooling jackets are sometimes required to counter the temperature rise in the extruder barrel during long periods of fast running, to keep the extrudate below the gel temperature of the viscosity enhancing agent being used. As a result, in some instances viscosity enhancing agents with higher gel temperatures are preferred to avoid this complication. Hence, the ability to use a type of viscosity enhancing agent that does not undergo thermal gelation (like hydroxyethyl cellulose (HEC)) would be a great advantage in certain applications.

The present invention seeks to ameliorate at least some of the disadvantages of the prior art or provide a commercial alternative thereto.

DISCLOSURE OF THE INVENTION

In a first aspect, the present invention provides an agent for treating an extrudable
5 cementitious material, comprising a viscosity enhancing agent and a dispersion agent in a quantity sufficient to increase the efficacy of the viscosity enhancing agent.

The applicant has found that by addition of a suitable dispersion agent, the efficacy of the viscosity enhancing agent can be increased. The reference to increasing the efficacy of the viscosity enhancing agent refers to the addition of the suitable dispersion
10 agent sufficient to provide one of three results

- i) maintaining extrudability with less viscosity enhancing agent as compared to the conventional dosage without dispersion agent,
- ii) maintaining extrudability with use of lower grade (cheaper) viscosity enhancing agent than is conventionally used, or
- 15 iii) improving extrudability for the same quantity of viscosity enhancing agent as compared to the conventional dosage.

Unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense
20 of "including, but not limited to".

In a second aspect, the present invention provides a cementitious formulation comprising a cementitious material, optionally with lime, silica, density modifiers, reinforcing fibres in water, and a viscosity enhancing agent and a dispersion agent in a quantity sufficient to increase the efficacy of the viscosity enhancing agent.

25 In a third aspect, the present invention provides for the use of one or more dispersion agents in the extrusion of a cementitious material for the purposes of increasing the efficacy of a viscosity enhancing agent used therein.

Dispersion agents, also known as plasticisers or super plasticisers, have long been used in the concrete industry to improve paste workability or to increase fluidity. The
30 attraction forces existing amongst the cement particles that cause agglomeration are neutralised by adsorption of anionic polymers. The dispersion of these cement particles

is related to the electrical repulsion produced by the absorption of the negatively charged group. This mechanism has been confirmed in sulphonated-type dispersion agents such as sulphonated melamine formaldehyde and sulphonated naphthalene formaldehyde.

The dispersion mechanism for acrylic polymers is believed to be ascribed to a steric
5 hindrance effect rather than electrostatic repulsion. These dispersion agents, however, have not been used as rheology modifiers in fibre reinforced cement slurry.

The applicant has found a surprising synergy between viscosity enhancing agents and dispersion agents. The combination of viscosity enhancing agent and dispersion agent is far superior in terms of rheology modification than either component alone. The
10 addition of the dispersion agent also allows use of a far broader range of viscosity enhancing agents than have otherwise been proposed. To explain, as mentioned above, the most common viscosity enhancing agents are hydroxypropylmethyl cellulose, hydroxyethylmethyl cellulose and methyl cellulose. These products are quite expensive and accordingly large additions are preferably avoided.

15 By combining the viscosity enhancing agent with a dispersion agent, the effectiveness of the viscosity enhancing agent is increased, thereby improving its extrudability, ie ability to flow under applied force, or reducing the quantity of viscosity enhancing agent required to maintain extrudability. Further, cheaper viscosity enhancing agents can be used such as lower grade hydroxypropylmethyl cellulose or hydroxyethyl
20 cellulose. These cheaper viscosity enhancing agents can be around half the cost of high grade cellulose ethers.

The current invention enables the forming of compositions with improved mouldability and workability or alternatively the reduction of cost by allowing the use of less viscosity enhancing agents and/or the use of lower (cheaper) grades of viscosity
25 enhancing agents. The addition of 0.05-0.5 wt. % of a dispersion agent, can result in the requirement for viscosity enhancing agents falling by ~20% and/or a less potent viscosity enhancing agent being used with equivalent or better extrudability than compositions with the conventional levels of viscosity enhancing agent.

As will be clear to persons skilled in the art, and as discussed above, increasing the
30 effectiveness of the viscosity enhancing agent to improve/maintain extrudability will also avoid or reduce common extrusion problems such as segregation, tearing, phase

separation, dewatering, etc. It may also result in an increase in structural integrity and better retention of the shape of the extrudate.

In some cases, the improvement in extrudability has been demonstrated by increasing the speed of extrusion. For example, some cementitious formulations
5 containing viscosity enhancing agent and optionally some dispersion agent may extrude but at a relatively low speed with a relatively high head pressure on the dye. The applicant has found that by addition of a suitable quantity of dispersion agent, the speed of extrusion can be increased markedly and the head pressure on the dye similarly reduced. Such results are normally achieved by increasing the quantity or grade of the
10 viscosity enhancing agent in the cementitious paste. It is quite unexpected that such improvements can be achieved by the simple addition of a dispersion agent.

Examples of high grade viscosity enhancing agents are high molecular weight cellulose ethers, for example alkylcellulose or hydroxyalkyl alkylcellulose. Low grade VEA's can be the same compounds at a lower molecular weight. Suitable viscosity
15 enhancing agents for use with the present invention include methyl cellulose, hydroxyethyl cellulose, hydroxyethylmethyl cellulose, hydroxypropylmethyl cellulose, carboxymethyl cellulose, ethyl cellulose, hydroxybutylmethyl cellulose, polyvinyl alcohol, clays, modified clays, Welan gum and other natural gums. The viscosity enhancing agent and/or dispersion agent can be added together or separately to the
20 cementitious slurry or indeed included in the dry formulation prior to slurry preparation. As will be clear to persons skilled in the art, it is important that the dispersion agent and viscosity enhancing agent are thoroughly mixed through the slurry to provide a homogeneous mix.

Suitable dispersion agents include sulphonated melamine formaldehyde,
25 sulphonated naphthalene formaldehyde, amino-sulphonate polymer, modified lignosulfonate materials and acrylic polymers such as copolymer of acrylic acid with acrylic ester, copolymers of acrylic acid with polycarboxylate ester and cross-linked acrylic polymers.

In a fourth aspect, the present invention provides a method of producing an agent
30 for treating an extrudable cementitious material comprising combining a viscosity

enhancing agent with a dispersion agent in a quantity sufficient to increase the efficacy of the viscosity enhancing agent.

In a fifth aspect, the present invention provides a method of treating a cementitious material for extrusion, said method comprising adding to the cementitious material a
5 viscosity enhancing agent and a dispersion agent in a quantity sufficient to increase the efficacy of the viscosity enhancing agent.

The invention further provides in a method for extruding a cementitious material, an improvement comprising adding a quantity of dispersion agents sufficient to increase the efficacy of a viscosity enhancing agent contained in said cementitious material.

10 As discussed above, it is important when extruding a cementitious paste or slurry that stringent rheological criteria are met while minimising the cost due to the use of viscosity enhancing agents.

In order to determine suitable quantities of viscosity enhancing agent and dispersion agent, or indeed conduct comparative analysis of different formulations, a
15 simple extrusion test may be conducted whereby a cementitious paste is provided including the viscosity enhancing agent and dispersion agent. The treated paste is then applied to a test die at a test pressure to confirm extrudability. As it will be clear to persons skilled in the art, exact quantities of viscosity enhancing agent and dispersion agent will depend on a number of factors including the type of agent used, the content of
20 the cementitious paste and indeed the extrusion equipment in which the cementitious paste will be used.

It is not entirely clear at this stage why the synergistic effect between the dispersion agent and viscosity enhancing agent is obtained. The effect of the synergy does differ, however, between various viscosity enhancing agents and dispersion agents. While in
25 some cases the efficacy of the viscosity enhancing agent has only been increased marginally, all mixtures have shown some synergistic effect and the applicant sees no basis on which the synergistic effect should not be maintained in a full scale operation.

The viscosity enhancing agent and dispersion agent can be added simultaneously or separately to the cementitious material. The viscosity enhancing agent and dispersion
30 agent can be added as dry solids, either before or after the addition of water to the other solid components. The viscosity enhancing agent and dispersion agent can also be

dispersed in water first and then added to the other solid components. Liquid, solid, solution, emulsion or suspension forms of viscosity enhancing agents and dispersion agents can be used.

It is also possible to provide the viscosity enhancing agent, dispersion agent and all
5 other components of the product including cementitious material, density modifiers, fibres etc dry mixed together for subsequent mixing with water to form a paste or slurry.

Alternatively, some of the solid components eg cementitious material, lime, silica, density modifiers etc may be dry mixed with the viscosity enhancing agent thoroughly. Water may then be added to pre-wet the mixture. The dispersion agent may then be
10 dissolved in the rest of the water and added to the solution to the mix. Mixing is generally not required for any longer than five minutes. Total wet mixing time should preferably not exceed 15 minutes. The resultant mixture is then kneaded for say around five minutes depending upon the effectiveness of the kneading facility. In this regard long kneading times should be avoided. The material is then suitable for use in the
15 extrusion apparatus.

In an alternative form, a cementitious slurry or paste may be provided with the desired consistency, with suitable quantities of viscosity enhancing agent and dispersion agent be subsequently added as powder, to the paste. In this instance, longer kneading time may be required to thoroughly mix the viscosity enhancing agent and dispersion
20 agent in the paste.

If desired, the viscosity enhancing agent and dispersion agent may be provided to the cementitious slurry or paste via separate components of the FRC mixture. To explain, it may be appropriate to pre-treat the reinforcing pulp fibre with a dispersion agent. The cementitious material could be pre-dosed with a viscosity enhancing agent
25 whereby it is combined with a dispersion agent upon mixing with the fibre.

It should also be understood that more than one viscosity enhancing agent and more than one dispersion agent may be used in the mixture.

The compositions formed in the above mentioned ways may be cured at ambient temperature and pressure or at higher temperatures and pressures. Curing methods such
30 as steaming at high temperatures or autoclaving at high temperatures and pressures are possible. Unlike the prior art, the resultant extruded cementitious material is suitable for

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entirely clear why this occurs, however, the applicant has found clear visible improvement in surface finish between extruded articles according to the present invention and those of the prior art. This is even true for articles with higher fibre contents ie 15% and above.

- 5 The present invention will now be described with reference to the following non-limiting examples:

EXAMPLE 1

- A composition was prepared according to the materials and proportions indicated in Table 1, the solid components blended in a high speed Eirich mixer and then kneaded
 10 together with the water in a Hobart mixer. The paste produced was then extruded into sheets 50mm wide and 10mm thick using a Handle laboratory extruder with 75mm barrel. For each type of viscosity enhancing agent, repeat experiments were carried out with different addition levels to ascertain the minimum required for good extrusion, surface finish and shape retention. Table 2 lists the viscosity enhancing agents and
 15 dispersion agents trialed with some detail as to their origin, chemistry and cost. Table 3 lists the addition levels of viscosity enhancing agents and combinations of viscosity enhancing agents and dispersion agents that have equivalent performance in extrusion moulding and enables comparisons of the effect of the dispersion agent.

Table 1

Material	Details	Amount used
Fibre	Bleached softwood Kraft pulp from Weyerhaeuser.	11% wt of solids
Cement	OPC Type 1 from Blue Circle Southern	Cement : Silica 60:40
Silica	200G milled quartz	Cement : Silica 60:40
Water		30% of total weight

20 Table 2

Type	Details	Cost
VEA1	Shin-Etsu 90SHV-WF Hydroxyethyl methyl cellulose (HEMC) (12,000 mPas, 1% solution @ 20° C, Brookfield)	US\$8.00/kg
VEA2	Wolff Walsrode Walocel VP-M20677 Hydroxyethyl methyl cellulose (HEMC) (75,000-85,000 mPas - 2% solution @ 20° C, Haake Rotovisko)	US\$7.41/kg
VEA3	Dow J75	US\$8.50/kg

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	Hydroxypropyl methyl cellulose (HPMC) (75,000 mPas, 2% sol. And 3000 mPas, 1% sol. @ 20°C. Ubbelohde tube)	
VEA4	Union Carbide Cellosize QP 100MH	US\$6.50/kg
	Hydroxyethyl cellulose (HEC) (4000-6000 mPas, 1% solution @ 25° C, Brookfield)	
VEA5	Dow J20	
	Hydroxypropyl methyl cellulose (HPMC) (20,000 mPas, 2% sol. And 900 mPas, 1% sol. @ 20°C, Ubbelohde tube)	
VEA6	Sigma Aldrich- 41,933-8	
	Carboxy methyl cellulose (CMC) Av Mol. Wt - 700,000 Degree of substitution = 0.9	
DA1	SKW Melment F15	US\$2.80/kg
	Sulfonated melamine formaldehyde (SMF)	

Table 3

	Amount required without DA1	Amount required with 0.2% DA1	Cost of formulation US\$/tonne	
			OLD	NEW
VEA1	1.5%	1.2%	158.22	145.38
VEA2	1.5%	1.2%	151.98	140.39
VEA3	1.75%	1.5%	163.89	149.92
VEA4	Inadequate performance	1.2%	-	132.77

EXAMPLE 2

- 5 A composition was prepared according to the materials and proportions specified in Table 4. The solid components were blended in a high speed Eirich mixer and subsequently mixed with a water/VEA solution in a Hobart mixer. The paste produced was then extruded into sheets 50mm wide and 10mm thick using a Handle laboratory extruder with 75mm barrel. For each type of viscosity enhancing agent, repeat
- 10 experiments were carried out with different addition levels to ascertain the minimum required for good extrusion, surface finish and shape retention. Table 6 shows the levels of viscosity enhancing agent required using the method of the new invention and without.

Table 4

Material	Details	Amount used
Fibre	Bleached softwood Kraft pulp from Weyerhaeuser.	9% wt. of solids
Cement	OPC Type 1 from Blue Circle Southern	Cement : Silica 60:40
Silica	200G milled quartz	Cement : Silica 60:40
Density	Low density calcium silicate hydrate	10% wt of solids
Modifier		
Water		38% of total weight (41% when VEA6 is used).

Table 5

	Amount required without DA1	Amount required with 0.3% DA1	Cost of Formulation US\$/tonne	
			OLD	NEW
VEA3	2%	1.8%	183.11	177.68
VEA4	Inadequate performance	1.8%	-	154.84
VEA5	Inadequate performance	2%	-	-
VEA6	Inadequate performance	2.2%	-	147.63*

* Estimated price

5 EXAMPLE 3

Two compositions, one containing VEA3 (Mix 1) and the other VEA4/DA1 (Mix 2) were prepared according to the materials and proportions specified in Table 6. VEA3 is a high grade HPMC and VEA4 is a cheaper HEC compound. For each, all the solid components were blended in a high speed Eirich mixer. The dry solids were then

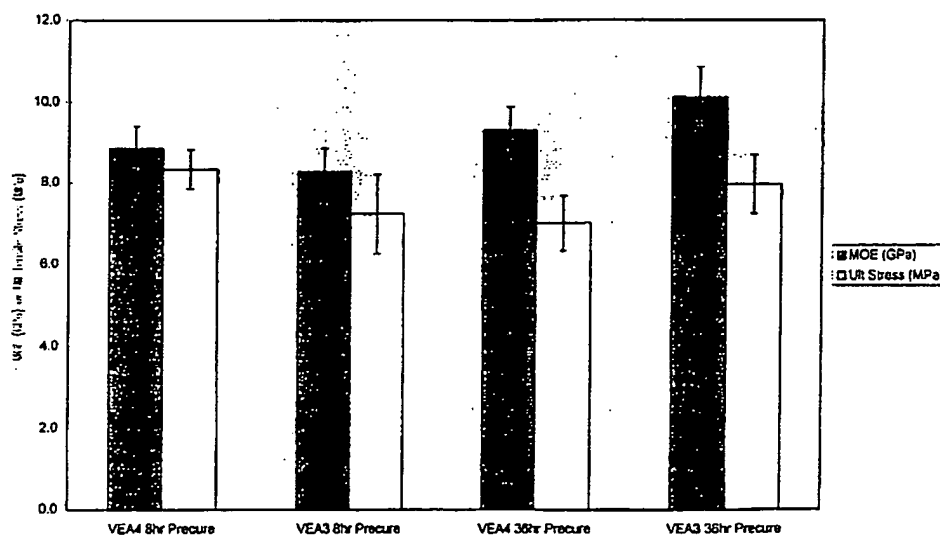
10 kneaded together with the water in a Hobart mixer till a homogenous paste was formed. The paste produced was then extruded into sheets 50mm wide and 10mm thick using a Handle laboratory extruder with 75mm barrel. Half the samples were pre-cured at ambient conditions for 8 hours and the other half at ambient conditions for 36 hours. The strips were then cured in an autoclave under saturated steam pressure at 177° C for 8

15 hours. The mechanical properties of the two compositions were tested, and Graph 1 shows the results. It can be seen that there is no significant difference in the measured mechanical properties between samples made with VEA3 and VEA4/DA1. It was also observed that the sample made with VEA4/DA1 had the better surface finish of the two.

Table 6

Material	Details	Amount used
Fibre	Bleached softwood Kraft pulp from Weyerhaeuser.	9% wt. of solids
Cement	OPC Type 1 from Blue Circle Southern	Cement : Silica 60:40
Silica	200G milled quartz	Cement : Silica 60:40
Density Modifier	PQ Extendspheres (hollow ceramic spheres, effective density ~0.7 g/cc)	10% wt of solids
Water		30% of total weight
VEA3	As in Table 2	2% in Mix 1
VEA4	As in Table 2	2% in Mix 2
DA1	As in Table 2	0.3% in Mix 2

Graph 1



5

EXAMPLE 4

A composition was prepared according to the materials and proportions indicated in Table 7, the solid components blended in a high speed Eirich mixer and then kneaded together with the water in a Hobart mixer. The paste produced was then extruded into sheets 50mm wide and 10 mm thick using Handlë laboratory extruder with a 75mm

barrel. Table 8 describes the viscosity enhancing agent and dispersion agent used and Table 9 shows the levels of viscosity enhancing agent required with and without the dispersion agent and demonstrates the synergy.

Table 7

Material	Details	Amount Used
Fibre	Bleached softwood Kraft pulp from Weyerhaeuser	9% wt of solids
Cement	OPC Type I from Blue Circle Southern	60:40 cement:silica
Silica	200G milled quartz	60:40 cement:silica
Density	Low density calcium silicate hydrate	30% wt of solids
Modifier		
Water		52% of total weight

Table 8

Type	Details	Cost
VEA 7	Rheolate 101 from Elementis Alkali swellable modified polyacrylate emulsion (15 Pa.s, 1% sol.@ 1 1/S (shear rate) and PH=7.0, 25 deg. C Brookfield)	US\$6.28/kg
DA1	SKW Melment F15 Sulfonated Melamine Formaldehyde (SMF)	US\$2.80/kg

Table 9

	Amount required without DA1	Amount required with 0.3% DA1	Cost of Formulation (US\$/tonne)	
			OLD	NEW
VEA 7	5.5%	4.5%	233.87	206.63

It will be understood by persons skilled in the art that the following embodiments are shown by way of example only and that other applications/embodiments may be developed without departing from the spirit or scope of the present invention.

CLAIMS

1. An agent for treating an extrudable cementitious material, comprising a viscosity enhancing agent and a dispersion agent in a quantity sufficient in increase the efficacy of the viscosity enhancing agent.
- 5 2. An agent as claimed in claim 1 wherein the viscosity enhancing agent is provided as 0.3-5% by weight of dry solids of the cementitious material and the dispersion agent is provided as 0.05-.05% by weight of dry solids of cementitious material.
3. An agent as claimed in claim 1 or 2 wherein the dispersion agent is added in a quantity sufficient to maintain extrudability of the cementitious material with a reduced
10 dosage of viscosity enhancing agent as compared to a conventional dosage.
4. An agent as claimed in claim 1 or 2, wherein the dispersion agent is added in a quantity sufficient to maintain extrudability of the cementitious material with a lower grade or cheaper viscosity enhancing agent as compared to a conventional dosage.
5. An agent as claimed in claim 1 or 2, wherein the dispersion agent is added in a
15 quantity sufficient to improve extrudability for a quantity of viscosity enhancing agent substantially equivalent to a conventional dosage.
6. An agent as claimed in any one of the preceding claims wherein the viscosity enhancing agent is a cellulose ether.
7. An agent as claimed in any one of the preceding claims wherein the viscosity agent
20 is hydroxy alkyl cellulose, hydroxy alkyl alkyl cellulose, carboxy alkyl cellulose or alkyl cellulose, or mixtures thereof.
8. An agent as claimed in any one of the preceding claims wherein the viscosity enhancing agent is selected from the group consisting of hydroxy propyl methyl

cellulose, hydroxy ethyl methyl cellulose, methyl cellulose, hydroxy ethyl cellulose, carboxy methyl cellulose, ethyl cellulose and hydroxy butyl methyl cellulose, or mixtures thereof.

9. An agent as claimed in any one of the preceding claims wherein the viscosity
5 enhancing agent is selecting from the group consisting of polyvinyl alcohols, gums include Welan gum, locust bean gum guar gum, sodium alginate, swellable alkali emulsions of acrylic co-polymers, clays or modified clays, polyethylene glycol and acrylic based polymers or mixtures thereof.
10. An agent as claimed in any one of the preceding claims wherein the dispersion
10 agent is a sulphonated type dispersion agent.
11. An agent as claimed in any one of the preceding claims wherein the dispersion agent is sulphonated melamine formaldehyde or sulphonated naphthalene formaldehyde.
12. A cementitious formulation comprising a cementitious material, optionally with lime, silica, density modifiers, reinforcing fibres and water, and a viscosity enhancing
15 agent and a dispersion agent in a quantity sufficient to increase the efficacy of the viscosity enhancing agent.
13. A cementitious formulation as claimed in claim 12 comprising 0.3-5% by weight of dry solids of viscosity enhancing agent and 0.05-0.5% by weight of dry solids of dispersion agent.
- 20 14. A cementitious formulation as claimed in claim 12 or 13 wherein dispersion agent is added in a quantity sufficient to maintain extrudability with a reduced dosage of viscosity enhancing agent as compared to a conventional dosage.

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15. A cementitious formulation as claimed in claim 12 or 13 wherein dispersion agent is added in a quantity sufficient to maintain extrudability with a lower grade or cheaper viscosity enhancing agent as compared to a conventional dosage.
16. A cementitious formulation as claimed in claim 12 or 13 wherein dispersion agent
5 is added in a quantity sufficient to improve extrudability for a quantity of viscosity enhancing agent substantially equivalent to a conventional dosage.
17. A cementitious formulation as claimed in any one of claims 12 to 16 wherein the viscosity enhancing agent is a cellulose ether.
18. A cementitious formulation as claimed in any one of claims 12 to 17 wherein the
10 viscosity agent is hydroxy alkyl cellulose, hydroxy alkyl alkyl cellulose, carboxy alkyl cellulose or alkyl cellulose, or mixtures thereof.
19. A cementitious formulation as claimed in any one of claims 12 to 18 wherein the viscosity enhancing agent is selected from the group consisting of hydroxy propyl methyl cellulose, hydroxy ethyl methyl cellulose, methyl cellulose, hydroxy ethyl
15 cellulose, carboxy methyl cellulose, ethyl cellulose and hydroxy butyl methyl cellulose, or mixtures thereof.
20. A cementitious formulation as claimed in any one of claims 12 to 19 wherein the viscosity enhancing agent is selecting from the group consisting of polyvinyl alcohols, gums include Welan gum, locust bean gum guar gum, sodium alginate, swellable alkali
20 emulsions of acrylic co-polymers, clays or modified clays, polyethylene glycol and acrylic based polymers or mixtures thereof.
21. A cementitious formulation as claimed in any one of claims 12 to 20 wherein the dispersion agent is a sulphonated type dispersion agent.

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22. A cementitious formulation as claimed in any one of claims 12 to 21 wherein the dispersion agent is sulphonated melamine formaldehyde or sulphonated naphthalene formaldehyde.

23. The use of one or more dispersion agents in the extrusion of a cementitious
5 material for the purposes of increasing the efficacy of a viscosity enhancing agent used therein.

24. A method of producing an agent for treating an extrudable cementitious material comprising combining a viscosity enhancing agent with a dispersion agent in a quantity sufficient to increase the efficacy of the viscosity enhancing agent.

10 25. A method as claimed in claim 24 wherein the viscosity enhancing agent is provided as 0.3-5% by weight of dry solids of the cementitious material and the dispersion agent is provided as 0.05-.05% by weight of dry solids of cementitious material.

26. A method as claimed in claim 24 or 25 wherein the dispersion agent is added in a
15 quantity sufficient to maintain extrudability of the cementitious material with a reduced dosage of viscosity enhancing agent as compared to a conventional dosage.

27. A method as claimed in claim 24 or 25, wherein the dispersion agent is added in a quantity sufficient to maintain extrudability of the cementitious material with a lower grade or cheaper viscosity enhancing agent as compared to a conventional dosage.

20 28. A method as claimed in claim 24 or 25, wherein the dispersion agent is added in a quantity sufficient to improve extrudability for a quantity of viscosity enhancing agent substantially equivalent to a conventional dosage.

29. A method as claimed in claim 24 or 25 wherein the viscosity enhancing agent is a cellulose ether.
30. A method as claimed in any one of claims 24 to 29 wherein the viscosity agent is hydroxy alkyl cellulose, hydroxy alkyl alkyl cellulose, carboxy alkyl cellulose or alkyl
5 cellulose, or mixtures thereof.
31. A method as claimed in any one of claims 24 to 30 wherein the viscosity enhancing agent is selected from the group consisting of hydroxy propyl methyl cellulose, hydroxy ethyl methyl cellulose, methyl cellulose, hydroxy ethyl cellulose, carboxy methyl cellulose, ethyl cellulose and hydroxy butyl methyl cellulose, or
10 mixtures thereof.
32. A method as claimed in any one of claims 24 to 31 wherein the viscosity enhancing agent is selecting from the group consisting of polyvinyl alcohols, gums include Welan gum, locust bean gum guar gum, sodium alginate, swellable alkali emulsions of acrylic co-polymers, clays or modified clays, polyethylene glycol and
15 acrylic based polymers or mixtures thereof.
33. A method as claimed in any one of claims 24 to 32 wherein the dispersion agent is a sulphonated type dispersion agent.
34. A method as claimed in any one of claims 24 to 33 wherein the dispersion agent is sulphonated melamine formaldehyde or sulphonated naphthalene formaldehyde.
- 20 35. A method as claimed in any one of claims 24 to 34 wherein the viscosity enhancing agent and dispersion agent are combined prior to treating the cementitious material.

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36. A method as claimed in any one of claims 24 to 35 wherein the viscosity enhancing agent and dispersion agent are combined insitu with the cementitious material.
37. A method of treating a cementitious material for extrusion, said method
5 comprising adding to the cementitious material a viscosity enhancing agent, and a dispersion agent in a quantity sufficient to increase the efficacy of the viscosity enhancing agent.
38. A method as claimed in claim 37 comprising 0.3-5% by weight of dry solids of viscosity enhancing agent and 0.05-0.5% by weight of dry solids of dispersion agent.
- 10 39. A method as claimed in claim 37 or 38 wherein dispersion agent is added in a quantity sufficient to maintain extrudability with a reduced dosage of viscosity enhancing agent as compared to a conventional dosage.
40. A method as claimed in any one of claims 37 to 39 wherein dispersion agent is added in a quantity sufficient to maintain extrudability with a lower grade or cheaper
15 viscosity enhancing agent as compared to a conventional dosage.
41. A method as claimed in any one of claims 37 to 40 wherein dispersion agent is added in a quantity sufficient to improve extrudability for the given quantity of viscosity enhancing agent substantially equivalent to a conventional dosage.
42. A method as claimed in any one of claims 37 to 41 wherein the viscosity
20 enhancing agent is a cellulose ether.
43. A method as claimed in any one of claims 37 to 42 wherein the viscosity agent is hydroxy alkyl cellulose, hydroxy alkyl alkyl cellulose, carboxy alkyl cellulose or alkyl cellulose, or mixtures thereof.

44. A method as claimed in any one of claims 37 to 43 wherein the viscosity enhancing agent is selected from the group consisting of hydroxy propyl methyl cellulose, hydroxy ethyl methyl cellulose, methyl cellulose, hydroxy ethyl cellulose, carboxy methyl cellulose, ethyl cellulose and hydroxy butyl methyl cellulose, or
5 mixtures thereof.
45. A method as claimed in any one of claims 37 to 44 wherein the viscosity enhancing agent is selecting from the group consisting of polyvinyl alcohols, gums include Welan gum, locust bean gum guar gum, sodium alginate, swellable alkali emulsions of acrylic co-polymers, clays or modified clays, polyethylene glycol and
10 acrylic based polymers or mixtures thereof.
46. A method as claimed in any one of claims 37 to 45 wherein the dispersion agent is a sulphonated type dispersion agent.
47. A method as claimed in any one of claims 37 to 46 wherein the dispersion agent is sulphonated melamine formaldehyde or sulphonated naphthalene formaldehyde.
- 15 48. In a method for extruding a cementitious material, the improvement comprising adding a quantity of dispersion agent sufficient to increase the efficacy of a viscosity enhancing agent contained in said cementitious material.
49. A method of forming a low density cementitious article comprising adding a cementitious material, density modifying additive, viscosity enhancing agent and
20 dispersion agent to water, extruding the resultant paste and curing the extruded article wherein the dispersion agent is added in a quantity sufficient to increase the efficacy of the viscosity enhancing agent.

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50. A method as claimed in claim 49 wherein prior to extrusion, lime, silica and/or fibre reinforcement may be added to the cementitious material.

51. A method as claimed in claim 49 or 50 wherein the density of the cured article is not greater than 1.2 grams per cm³.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/01001

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : C04B 24/00, 24/10, 24/16, 24/18, 24/22, 24/24, 24/26, 24/28, 24/38, 22/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC C04B 24/-, 22/-, 16/06, 14/38		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU: IPC as above.		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96/40598 (THE NUTRASWEET COMPANY) 19 December 1996 Whole Document	1-51
X	US 5470383 (Shermann et al.) 28 November 1995 Whole Document	1-51
X	US 5453123 (Burge et al.) 26 September 1995 Whole Document	1-51
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 6 October 2000		Date of mailing of the international search report 10 OCT 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer CHRIS BURTON Telephone No : (02) 6283 2559

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/01001

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5387626 (Böhme-Kovac et al.) 7 February 1995 Whole Document	1-51
X	US 5352290 (Takeshita et al.) 4 October 1994 Whole Document	1-51
X	JP 06-127992 (KAO CORP) 10 May 1994 Whole Document	1-51
X	AU 13067/92 (HOECHST AKTIENGESELLSCHAFT) 24 September 1992 Whole Document	1-51
X	US 4846889 (Meyer) 11 June 1989 Whole Document	1-51
X	AU 55929/86 (THE DOW CHEMICAL COMPANY) 30 October 1986 Whole Document	1-51
X	AU 44948/85 (SANDOZ AG) 16 January 1986 Whole Document	1-51

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU00/01001

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
WO	96/40598	CA	2223723	EP	830327	WO	96/40599
		US	6106603				
US	5470383	CA	2126546	DE	4320508	EP	630871
		JP	7166150				
US	5453123	CA	2110658	EP	602541	JP	6219799
US	5387626	BR	9203431	CZ	9202743	EP	530768
		JP	5201756	MX	9205038		
US	5352290	CN	1075471	EP	540413	JP	5147995
JP	06127992	-					
AU	13067/92	BR	9200950	EP	504870	JP	5186637
		US	5432215				
US	4846889	BR	8900440	EP	327351	JP	1279936
AU	55929/86	BR	8601801	EP	200471	FI	861725
		JP	61281055	NO	861593		
AU	44948/85	EP	188471	JP	61006163	NO	860618
		WO	8600291	ZA	8504666	BR	8504666
		ES	544345	JP	61086455		
END OF ANNEX							

autoclave curing. This is a further distinction over the prior art which use synthetic fibres unsuitable for autoclaving.

The exact regime of curing, such as pre-cure times, temperatures, pressures and cure times must be optimised for the specific formulation. As is well known, to achieve
5 optimum strength it is important to avoid the cementitious products drying out during curing.

Compositions formed using the method of this invention show no adverse effects in terms of physical or mechanical properties during curing or afterwards when compared to specimens made with conventional techniques using high grade viscosity
10 enhancing agents. In fact the use of dispersion agents appears to aid the forming of a superior surface finish.

The disclosed method and treatment agent are also particularly suitable for producing low density composite articles, that contain a high proportion of density modifying additives. Examples of such additives would be perlite, vermiculite, low
15 density calcium silicate hydrate, ceramic hollow spheres, fly-ash etc. This invention can also be used with the addition of air entraining agents to modify density. Densities of 1.2 g/cm^3 or below may be achieved using the present invention.

In still a further aspect, the present invention provides a method of forming a low density cementitious article comprising adding a cementitious material, density
20 modifying additive, a viscosity enhancing agent and dispersion agent to water, extruding the resultant paste and curing the extruded article, wherein the dispersion agent is added in a quantity sufficient to increase the efficacy of the viscosity enhancing agent.

This invention also is suitable for compositions containing a variety of reinforcing fibres. Examples of such fibres would be wood pulp (cellulose) fibres, asbestos fibres,
25 polymer fibres, glass or metal fibres. This is another advantage arising from the present invention. The prior art extrusion techniques are limited to particular fibres and particular fibre contents. The present invention allows an operator to choose the type and quantity of fibre to specifically match the article to its desired use eg up to around 25% vol.

30 Further, it has been found that the addition of viscosity enhancing agent and dispersion agent provides an extruded product with an improved surface finish. It is not